

3 ELECTROCHEMICAL STUDIES IN NON-AQUEOUS SOLVENTS. ^{2π₂#} VI ACETONITRILE. 6

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Introduction

This is the first in a group of reports in which certain electrochemical data (and closely related auxiliary data) are critically reviewed for various non-aqueous solvents. The principal emphasis has been on electrochemical potentials as derived from more or less traditional cell measurements or polarographic measurements. For some solvents, these data may be usefully extended by calculations of potentials from thermodynamic data. Since auxiliary data such as acid ionization constants, activity coefficients, solubility products, and transport numbers are often relevant to experimental determinations of potentials or to subsequent use of potentials, we have either summarized such data or provided references to appropriate sources.

This report is concerned with acetonitrile, which is the most common of the nitrile solvents. It is both a weaker base and a weaker acid than water¹ and appropriate acidity studies have shown it to be a good differentiating solvent².

Some physical properties of acetonitrile are summarized in Table I.

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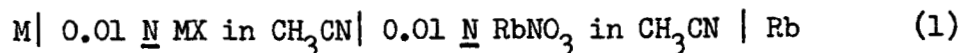
TABLE I

Physical Properties of Acetonitrile

molecular weight	41.05 gm mole ⁻¹
density at 25°C (ref. 3)	0.7768 gm ml ⁻¹
normal boiling point (ref. 3)	81.6°C
normal freezing point (ref. 3)	-45.7°C
viscosity at 25°C (ref. 3)	0.34 cp
specific conductivity at 25°C (ref. 3)	~ 6 x 10 ⁻⁸ ohm ⁻¹ cm ⁻¹
dielectric constant at 25°C (ref. 3)	36.0
heat of fusion at triple point, -43.83°C (ref. 4)	1.952 kcal mole ⁻¹
heat of vaporization at 25°C (ref. 4)	7.941 kcal mole ⁻¹
refractive index at 20°C, n _D (ref. 5)	1.3436

Cell Measurements

In spite of considerable interest in acetonitrile as a solvent, relatively few potential measurements have been made on cells with (presumably) reversible electrodes. The first and to date most extensive measurements were made by Pleskov^{6,7}. In 1947 Pleskov⁶ reported "standard" potentials for cells that can be represented by

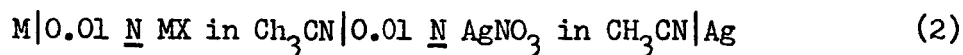


Although results given by Pleskov and cited in Table II below are often quoted, neither the raw data nor complete details of calculation of reported standard potentials from measured potentials appear to be available.

TABLE II
Standard Potentials⁶ for Cell (1) at 25°C

M MX	E° (Rb/Rb ⁺ ref.)	E° (H ₂ /H ⁺ ref.)
Li Li ⁺	-0.006 V -0.006 V	-3.23
Rb Rb ⁺	0.00	-3.17
K K ⁺	+0.01	-3.16
Cs Cs ⁺	0.01	-3.16
Na Na ⁺	0.30	-2.87
Ca Ca ⁺⁺	0.42	-2.75
Zn Zn ⁺⁺	2.43	-0.74
Cd Cd ⁺⁺	2.70	-0.47
Cu Cu ⁺	2.79	-0.38
Cu Cu ⁺⁺	2.89	-0.28
Pb Pb ⁺⁺	3.05	-0.12
H ₂ H ⁺	3.17	0.00
Ag Ag ⁺	3.40	+0.23
Hg Hg ⁺⁺	3.42	+0.25

In 1948 Pleskov⁷ reported results of measurements on cells represented by

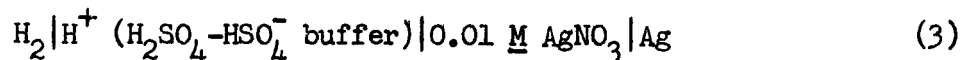


The results obtained with cell (2) were stated to be in good agreement with those obtained with cell (1), except for ZnCl₂, CdI₂ and HgBr₂. Distinction between measured cell potentials and calculated (with activity coefficients) standard potentials is not entirely clear.

Conductivity data for a few salts and solubilities for many salts are reported in this paper⁷.

Papon and Jacq⁸ have studied the $\text{Ag}|\text{Ag}^+$ electrode vs the $\text{H}_2|\text{H}^+$ electrode in various $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ mixtures and have extrapolated to pure CH_3CN to obtain a potential of 0.23 v, which agrees with the value calculated from Pleskov's results^{6,7}.

Kolthoff and Thomas⁹ have made measurements on cells that can be represented by



Their results have not been compared with Pleskov's^{6,7} results nor are relevant activity data available to permit quantitative comparison.

Kolthoff and Thomas⁹ have also made measurements in which various electrodes [ferrocene|ferrocinium and tris(o-phenanthroline)iron(II)-(III)] were compared to the aqueous standard calomel electrode.

Standard potentials were determined for these same electrodes vs $\text{Ag}|\text{Ag}^+$ in acetonitrile. A few conductivity data are also cited.

Kolthoff and Thomas⁹ have attempted to evaluate liquid junction potentials in order to compare electrode potentials for acetonitrile with those for the same electrodes in water. This important problem, which cannot be solved by purely thermodynamic means, has been reviewed recently by Strehlow¹⁰, who also cites substantially the same potentials as given in Table II. In an earlier review¹¹, Strehlow used solubility data in calculating 0.5₈, 0.4₇ and 0.0₇ v ($\text{H}_2|\text{H}^+$ ref) for the $\text{Cl}^-|\text{Cl}_2$, $\text{Br}^-|\text{Br}_2$ and $\text{I}^-|\text{I}_2$ electrodes.

Polarographic Measurements

There have been several polarographic investigations of metal ions in acetonitrile. A variety of reference electrodes, each with its own advantages and disadvantages, have been used. Internal reference electrodes of the second kind, such as $\text{Ag}|\text{AgX}$ or $\text{Hg}|\text{Hg}_2\text{X}_2$ (mercury pool electrodes), provide relative potentials for a given solvent without complications due to liquid junction potentials. Experimental difficulties have been experienced because of potential drift^{1,12}, electrode polarization¹³ and solubility of the electrode salt in solutions containing excess halide^{1,13}.

A number of workers have used external reference electrodes, which effectively avoid the problems mentioned above while introducing more or less uncertain junction potentials. For example, Popov and Geske¹³ used a $\text{Ag}|\text{AgCl}$ (sat'd in CH_3CN) external reference electrode with chloride concentration controlled with trimethylethyl ammonium chloride. Despite the introduction of an uncertain liquid junction potential, Kolthoff, Coetzee et al^{1,9,14,15} have used successfully an aqueous saturated calomel electrode with a KCl agar salt bridge.

Polarographic half wave potentials (dropping mercury electrode with various supporting electrolytes) for metal ions in acetonitrile are summarized in Table III.

TABLE III

Half Wave Potentials for Cations in Acetonitrile

(dropping mercury electrode)

Cation	Supporting Electrolyte ^a	Reference Electrode	$E_{1/2}$	Reference
H^+	Bu_4NClO_4	$Ag AgNO_3^b$	-0.78	13
Li^+	Bu_4NI	Hg pool	-1.42 ^c	16
	Bu_4NClO_4	Hg pool	-2.33	16
	Bu_4NClO_4	$Ag AgNO_3^b$	-2.26	13
	Et_4NClO_4	SCE(aq)	-1.95 ^c	1
Na^+	Bu_4NI	Hg pool	-1.25 ^d	16
	Bu_4NClO_4	$Ag AgNO_3^b$	-2.14	13
	Et_4NClO_4	SCE(aq)	-1.85 ^d	1
	Et_4NClO_4	SCE(aq)	-1.85 ^d	15
	Bu_4NI	SCE(aq)	-1.85 ^d	1
K^+	Bu_4NI	Hg pool	-1.34 ^d	16
	Bu_4NClO_4	$Ag AgNO_3^b$	-2.24	13
	Bu_4NI	SCE(aq)	-1.94 ^d	1
Rb^+	Bu_4NI	Hg pool	-1.36 ^d	16
	Bu_4NI	SCE(aq)	-1.95 ^d	1

TABLE III continued

Cation	Supporting Electrolyte ^a	Reference Electrode	$E_{1/2}$	Reference
Cs ⁺	Bu ₄ NI	Hg pool	$\sim -1.34^e$	16
Be ⁺⁺	Et ₄ NCIO ₄	SCE(aq)	-1.6^{cf}	14
Mg ⁺⁺	Bu ₄ NI	Hg pool	-1.16	16
	Et ₄ NCIO ₄	SCE(aq)	-1.84^c	14
Ca ⁺⁺	Bu ₄ NI	Hg pool	-1.24	16
	Bu ₄ NCIO ₄	Ag AgNO ₃ ^b	-2.14	13
	Et ₄ NCIO ₄	SCE(aq)	-1.82^{cf}	1
Sr ⁺⁺	Et ₄ NCIO ₄	SCE(aq)	-1.76^c	1
	Bu ₄ NCIO ₄	Ag AgNO ₃ ^b	$\sim -2.08^e$	13
Ba ⁺⁺	Et ₄ NCIO ₄	SCE(aq)	-1.63^c	1
	Bu ₄ NCIO ₄	Ag AgNO ₃ ^b	-1.92	13
Al ⁺⁺⁺	Et ₄ NCIO ₄	SCE(aq)	-1.42^f	14
	Bu ₄ NCIO ₄	Ag AgNO ₃ ^b	-1.64^f	13
Tl ⁺	Bu ₄ NCIO ₄	Ag AgNO ₃ ^b	-0.55	13
	Et ₄ NCIO ₄	SCE(aq)	-0.27	15

TABLE III continued

Cation	Supporting Electrolyte ^a	Reference Electrode	$E_{1/2}$	Reference
Sn ⁺⁺	Bu ₄ NClO ₄	Ag AgNO ₃ ^b	-0.23	13
Pb ⁺⁺	Bu ₄ NClO ₄	Hg pool	-0.44 ^f	16
	Bu ₄ NClO ₄	Ag AgNO ₃ ^b	-0.33	13
Ti(IV)	—	—	— ^g	17
Cr ⁺⁺⁺	NaClO ₄	SCE(aq)		14
Cr ⁺⁺⁺ → Cr ⁺⁺			0.0 ^f	
Cr ⁺⁺ → Cr			-1.12 ^f	
	Bu ₄ NClO ₄	Ag AgNO ₃ ^b		13
Cr ⁺⁺⁺ → Cr ⁺⁺			~-0.03 ^f	
Cr ⁺⁺ → Cr			-1.39 ^f	
Mn ⁺⁺	Bu ₄ NClO ₄	Ag AgNO ₃ ^b	-1.40 ^f	13
	NaClO ₄	SCE(aq)	-1.12 ^{df}	14
Fe ⁺³	NaClO ₄	SCE(aq)		14
Fe ⁺⁺⁺ → Fe ⁺⁺			— ^{fh}	
Fe ⁺⁺ → Fe			-1.00 ^f	
	Bu ₄ NClO ₄	Ag AgNO ₃ ^b		13
Fe ⁺⁺⁺ → Fe ⁺⁺			<0.36 ^f	
Fe ⁺⁺ → Fe			-1.33 ^f	

TABLE III continued

Cation	Supporting Electrolyte ^a	Reference Electrode	E _{1/2}	Reference
Fe ⁺⁺	Bu ₄ NClO ₄	Ag AgNO ₃ ^b	-1.33 ^f	13
Fe(C ₅ H ₅) ₂ ⁺ Fe(C ₅ H ₅) ₂	Et ₄ NClO ₄	SCE(aq)	-0.38 ^d	9
Co ⁺⁺	NaClO ₄	SCE(aq)	-0.65 ^f	14
	Bu ₄ NClO ₄	Ag AgNO ₃ ^b	-0.96 ^f	13
Ni ⁺⁺	NaClO ₄	SCE(aq)	-0.33 ^{df}	14
Cu ₂ ⁺⁺	Bu ₄ NI	Hg pool	— ^e	16
Cu ⁺⁺	Bu ₄ NClO ₄	Hg pool		16
Cu ⁺⁺ → Cu ⁺			~-0.14 ^{ef}	
Cu ⁺ → Cu			-0.98 ^f	
	NaClO ₄	SCE(aq)		14
Cu ⁺⁺ → Cu ⁺			— ^{fh}	
Cu ⁺ → Cu			-0.36 ^{df}	
	Bu ₄ NClO ₄	Ag AgNO ₃ ^b		13
Cu ⁺⁺ → Cu ⁺			< 0.36 ^{fh}	
Cu ⁺ → Cu			-0.62 ^f	
Ag ⁺	NaClO ₄	SCE(aq)	0.32 ^d	14
	Bu ₄ NClO ₄	Ag AgNO ₃ ^b	0.13	13
	Et ₄ NClO ₄	SCE(aq)	0.42 ^d	15

TABLE III continued

Cation	Supporting Electrolyte ^a	Reference Electrode	$E_{1/2}$	Reference
Zn^{++}	Bu_4NClO_4	Hg pool	-1.07^f	16
	Bu_4NClO_4	$Ag AgNO_3^b$	-0.91^f	13
	$NaClO_4$	SCE(aq)	-0.70^f	1
	Et_4NClO_4	SCE(aq)	-0.70^f	1
Cd^{++}	Bu_4NClO_4	Hg pool	-0.61^f	16
	$NaClO_4$	SCE(aq)	-0.27^f	1
	Bu_4NClO_4	$Ag AgNO_3^b$	-0.55	13
Hg^{++}	Bu_4NClO_4	$Ag AgNO_3^b$	$<0.36^f$	13
NH_4^+	Et_4NClO_4	SCE(aq)	-1.83	1
Sm^{+++}	Et_4NClO_4	SCE(aq)		14
$Sm^{+++} \rightarrow Sm^{++}$			-1.62^d	
$Sm^{++} \rightarrow Sm$			i	
	Et_4NClO_4	SCE(aq)		15
$Sm^{+++} \rightarrow Sm^{++}$			-0.98^d	
$Sm^{++} \rightarrow Sm$			-1.69	
	Et_4NClO_4	SCE(aq) ^j		18
$Sm^{+++} \rightarrow Sm^{++}$			-1.04	
$Sm^{++} \rightarrow Sm$			-1.55	

TABLE III continued

Cation	Supporting Electrolyte ^a	Reference Electrode	$E_{1/2}$	Reference
Eu ⁺⁺⁺	Et ₄ NClO ₄	SCE(aq)		14
Eu ⁺⁺⁺ → Eu ⁺⁺			0.15 ^d	
Eu ⁺⁺ → Eu			-1.67	
	Et ₄ NClO ₄	SCE(aq) ^j		18
Eu ⁺⁺⁺ → Eu ⁺⁺			0.10	
Eu ⁺⁺ → Eu			-1.62	
Yb ⁺⁺⁺	Et ₄ NClO ₄	SCE(aq)		14
Yb ⁺⁺⁺ → Yb ⁺⁺			-0.57	
Yb ⁺⁺ → Yb			-1.69	
	Et ₄ NClO ₄	SCE(aq) ^j		18
Yb ⁺⁺⁺ → Yb ⁺⁺			-0.60	
Yb ⁺⁺ → Yb			-1.58	
Nd ⁺⁺⁺	Et ₄ NClO ₄	SCE(aq) ^j		18
Nd ⁺⁺⁺ → Nd			-1.45	

Table III notes

- The concentration of the supporting electrolyte is 0.1 M.
- Popov and Geske¹³ used a Ag|AgCl (in CH₃CN) reference electrode for their polarographic measurements, but reported their results with respect to the Ag|0.01 M AgNO₃ (in CH₃CN) electrode.

Table III Notes continued

- c. Well-defined wave, but not reversible.
- d. Reversible wave.
- e. Maximum (not suppressible).
- f. $\text{Be}(\text{ClO}_4)_2 \cdot 4 \text{ aq}$; $\text{Ca}(\text{ClO}_4)_2 \cdot 6 \text{ aq}$; $\text{Al}(\text{ClO}_4)_3 \cdot 9 \text{ aq}$; $\text{Al}(\text{ClO}_4)_3 \cdot 6 \text{ aq}$;
 $\text{Pb}(\text{ClO}_4)_2 \cdot 3 \text{ aq}$; $\text{Cr}(\text{ClO}_4)_3 \cdot 6 \text{ aq}$; $\text{Mn}(\text{ClO}_4)_2 \cdot 6 \text{ aq}$; $\text{Fe}(\text{ClO}_4)_3 \cdot 6 \text{ aq}$;
 $\text{Fe}(\text{ClO}_4)_2 \cdot 6 \text{ aq}$; $\text{Co}(\text{ClO}_4)_2 \cdot 6 \text{ aq}$; $\text{Ni}(\text{ClO}_4)_2 \cdot 6 \text{ aq}$; $\text{Cu}(\text{ClO}_4)_2 \cdot x \text{ aq}$;
 $\text{Cu}(\text{ClO}_4)_2 \cdot 6 \text{ aq}$; $\text{Cu}(\text{ClO}_4)_2 \cdot 6 \text{ aq}$; $\text{Zn}(\text{ClO}_4)_2 \cdot 4 \text{ aq}$; $\text{Zn}(\text{ClO}_4)_2 \cdot 6 \text{ aq}$;
 $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{ aq}$; $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{ aq}$; $\text{Cd}(\text{ClO}_4)_2 \cdot 4 \text{ aq}$; $\text{Cd}(\text{ClO}_4)_2 \cdot 6 \text{ aq}$;
 $\text{Hg}(\text{ClO}_4)_2 \cdot 3 \text{ aq}$.
- g. Current-potential curves for a number of titanium halide and thiocyanate systems are reported.
- h. Not a true wave.
- i. No wave obtained.
- j. Cokal and Wise¹⁸ used a $\text{Ag}|\text{Ag}^+$ (in CH_3CN) reference electrode for their polarographic measurements, but reported their results with respect to the $\text{SCE}(\text{aq})$.

Coetzee, McGuire and Hedrick¹⁵ have reported one method for comparison of polarographic half wave potentials obtained with different reference electrodes and/or different supporting electrolytes. In the following paragraphs we cite some specific comparisons of data in Table III to illustrate several points.

The differences between the Li^+/Na^+ half wave potentials are 0.17, 0.12 and 0.10 v from references 16, 13 and 1, respectively. The spread of 0.07 v must be attributed to some combination of experimental error and effect of differences in supporting electrolyte. The differences between the K^+/Rb^+ half wave potentials are 0.02 and 0.01 v from references 16 and 1, respectively. Similarly, the differences between Na^+/K^+ half wave potentials are 0.09, 0.10 and 0.09 v from references 16, 13 and 1, respectively. From these comparisons and similar comparisons for the other alkali metal ions, we conclude that either the reported half wave potential for Li^+ determined with the Hg pool reference electrode (ref. 16) is too negative by a few hundredths of a volt or the effect of the anion (iodide or perchlorate) in the supporting electrolyte is unusually large for Li^+ .

Another interesting comparison involves the Mg^{++} and Na^+ half wave potentials. The difference between potentials taken from references 16 and 14 amounts to 0.09 and 0.01 v. Since the half wave potentials in Table III show that the supporting electrolyte has little effect on Na^+ , we must conclude that the spread in the above differences is due either to experimental error or to interaction of the supporting electrolyte with Mg^{++} . Similar comparisons for a number

of other elements indicate that there are certainly experimental difficulties and probably errors associated with the Hg pool electrode. These comparisons for several elements also confirm the expectation that the nature of the supporting electrolyte (particularly the anion) is more important for +2 ions than for +1 ions.

Appropriate comparisons like those above indicate that there are discrepancies of 0.05 μ or more between results of various investigators for the following: Al^{+++} , Pb^{++} , $\text{Cr}^{+++}|\text{Cr}^{++}$, Fe^{++} , Co^{++} , Cu^{+} , Ag^{+} , Zn^{++} , $\text{Sm}^{+++}|\text{Sm}^{++}$, Sm^{++} , $\text{Eu}^{+++}|\text{Eu}^{++}$, Eu^{++} , and Yb^{++} . The most negative half wave potential for $\text{Sm}^{+++}|\text{Sm}^{++}$ (ref. 14) appears to be in error, since two later investigators (refs. 15 and 18) are in fair agreement on a considerably less negative value. Several of the discrepancies for other ions are probably due to errors associated with the Hg pool reference electrode.

Coetzee and Kolthoff²⁹ have found that there are two waves in pure CH_3CN (-0.75 and -1.4 μ , versus aqueous SCE) at the dropping mercury electrode and interpret these values in terms of weak acidic properties of acetonitrile.

Although the dropping mercury electrode (DME) that is traditional in polarography has been used much for investigation of acetonitrile systems as indicated by the data in Table III, the rotating platinum electrode (RPE) offers some advantages for study of non-aqueous solvent systems. A discussion of these advantages, along with a review of many important experimental techniques relevant to investigation of acetonitrile and other non-aqueous solvents, has been prepared by Popov¹⁹.

Half wave potentials for various metal ions in acetonitrile as determined with the rotating platinum electrode are summarized in Table IV. All of these potentials were determined by Kolthoff and Coetzee¹⁴, who used the SCE(aq) reference electrode and NaClO_4 as supporting electrolyte.

Several investigators^{14,20,21} have obtained half wave potentials for various halides in acetonitrile, all using the rotating platinum electrode and various perchlorates as supporting electrolyte. Reasonable, but not entirely certain, comparison between half wave potentials obtained with different reference electrodes indicates that the results of different investigators are in fair agreement. Although we summarize the half wave potential data in Table V, readers of this report should consult the original papers for further information since some of the reported potentials are markedly concentration dependent and some of the electrode reactions are uncertain. Other potentials for mixed halide species are included in the cited references.

Popov and Geske²¹ and Nelson and Iwamoto²² have discussed calculation of standard potentials from half wave potentials.

Nelson and Iwamoto³⁰ have investigated the reversible 4,7-dimethyl-1,10-phenanthroline ferric|4,7-dimethyl-1,10-phenanthroline ferrous couple at the rotating platinum electrode with LiClO_4 supporting electrolyte. They discuss the half wave potential (0.86 v, SCE) in relation to liquid junction potentials and earlier work of Pleskov and Strehlow.

There have been a considerable number of polarographic investigations of organic compounds in acetonitrile. These investigations have been

TABLE IV

Half Wave Potentials for Metal Ions in Acetonitrile¹⁴

(rotating platinum electrode)

Ion ^{ab}	$E_{1/2}$
Ag^+	0.1
Cd^{++}	-0.5
Zn^{++}	-0.9
Hg^{++}	
$\text{Hg}^{++} \text{Hg}_2^{++}$	0.7
$\text{Hg}_2^{++} \text{Hg}$	0.5
Cu^{++}	
$\text{Cu}^{++} \text{Cu}^+$	1.0
$\text{Cu}^+ \text{Cu}$	-0.5
$\text{Fe}^{+++} \text{Fe}^{++}$	1.1
$\text{Fe}^{++} \text{Fe}^{+++}$	1.6

- a. The supporting electrolyte was NaClO_4 (0.2 M for Fe potentials and 0.1 M for the others). The external aqueous saturated calomel electrode was used for reference.
- b. Except for AgClO_4 , hydrated perchlorates were used.

TABLE V

Half Wave Potentials for Halides in Acetonitrile

(rotating platinum electrode)

Compound	Supporting Electrolyte ^a	Reference Electrode	E _{1/2}	Reference
LiCl	Et ₄ NClO ₄	SCE(aq)		14
Cl ⁻ Cl ₃ ⁻			1.1	
Cl ₃ ⁻ Cl ₂			1.7	
Et ₄ NBr	Et ₄ NClO ₄	SCE(aq)		14
Br ⁻ Br ₃ ⁻			0.7	
Br ₃ ⁻ Br ₂			1.0	
Et ₄ NBr	LiClO ₄	Ag AgNO ₃ ^b		20
Br ⁻ Br ₃ ⁻			0.42	
Br ₃ ⁻ Br ₂			0.71	
? ?			1.42	
Bu ₄ NBr ₃	LiClO ₄	Ag AgNO ₃ ^b		20
Br ₃ ⁻ Br ⁻			0.2	
Br ₃ ⁻ Br ₂			0.67	
? ?			1.43	
Br ₂	LiClO ₄	Ag AgNO ₃ ^b		20
Br ₃ ⁻ Br ⁻			~0.0	
Br ₂ Br ₃ ⁻			0.58	

TABLE V continued

Compound	Supporting Electrolyte ^a	Reference Electrode	E _{1/2}	Reference
NaI	Et ₄ NClO ₄	SCE(aq)		14
I ⁻ I ₃ ⁻			0.3	
I ₃ ⁻ I ₂			0.6	
NaI	LiClO ₄	Ag AgNO ₃ ^b		21
I ⁻ I ₃ ⁻			-0.01	
I ₃ ⁻ I ₂			0.31	
? ?			1.05	
? ?			1.82	
Me ₄ N ⁺ I ₃ ⁻	LiClO ₄	Ag AgNO ₃ ^b		21
I ⁻ I ₃ ⁻			-0.18	
I ₃ ⁻ I ₂			0.32	
? ?			1.08	
? ?			1.80	
I ₂	LiClO ₄	Ag AgNO ₃ ^b		21
I ⁻ I ₃ ⁻			-0.16	
I ₃ ⁻ I ₂			0.32	
? ?			—	
? ?			1.79	

a. Supporting electrolyte is 0.10 M

b. See note b, Table III.

primarily concerned with gaining knowledge about mechanisms of electrochemical reactions, identification of products of electrochemical reactions, and with development of improved methods for carrying out electrochemical preparations. For purposes of this review, it seems most appropriate to cite a number of references that report much of the important work and themselves give references to earlier work.

Wawzonek et al²³ have reported results of investigations of aromatic olefins and hydrocarbons, aromatic ketones and aldehydes, quinones, α,β unsaturated carbonyl compounds, various methyl halides, halobenzenes, benzyl halides, and related compounds. Solon and Bard²⁴ have studied the electroreduction and oxidation of diphenylpicrylhydrazyl (a stable free radical) in acetonitrile by a variety of techniques. Hansen, Toren and Young²⁵ have studied the relation of charge-transfer properties to potentials for some nitro compounds. Case, Hush, Parsons and Peover²⁶ have reported potentials for anthracene and other "alternant" aromatics. Gough and Peover²⁷ have surveyed potentials for a considerable number of aromatic compounds in acetonitrile. Anodic reactions of aliphatic amines have been investigated by Mann²⁸.

Acid Base Equilibria and Potentials

Coetzee and Kolthoff²⁹ have reported half wave potentials for several acids in acetonitrile. These measurements were made with the dropping mercury indicator electrode, an aqueous SCE reference and Et_4NClO_4 supporting electrolyte. Half wave potentials are listed in Table VI. Since none of the observed waves was completely reversible,

TABLE VI

Half Wave Potentials for Acids in Acetonitrile²⁹

Acid	$E_{1/2}$
perchloric	-0.70
hydrobromic	-0.90
2,5-dichloroanilinium	-1.00
hydrochloric	-1.06
p-toluenesulfonic	-1.20
sulfuric	-1.20
2,5-diethylanilinium	-1.43
fluorovaleric($C_5F_{11}CO_2H$)	\sim -1.5
oxalic	-1.55
phosphoric	-1.75
benzoic	-2.1
acetic	-2.3
bioxalate ion	no wave

no quantitative statements about acid strength were possible. Coetzee and Kolthoff do point out, however, that perchloric acid behaves like a typical strong acid and that sulfuric, oxalic and phosphoric acids behave as monobasic acids in these investigations.

Kilpatrick and Kilpatrick³¹ and Usanovich and Dulova³² have reported relative acid strengths of a considerable number of organic acids in acetonitrile. More recently, Kolthoff, Coetzee and others have been able to evaluate equilibrium constants for various acid-base equilibria in acetonitrile.

Coetzee and Padmanabhan³³ have determined that the autoprotolysis constant for acetonitrile is 3×10^{-27} . A glass electrode with buffered acetonitrile solutions was used for these measurements.

Kolthoff, Bruckenstein and Chantooni³⁴ have reported equilibrium constants for HBr, H_2SO_4 , HNO_3 , HCl and picric acid, and have also confirmed that perchloric acid is completely dissociated in dilute solution in acetonitrile.

Various equilibria that involve acids, bases and salts have been investigated and appropriate equilibrium constants reported as summarized briefly below:

Amines: references 35, 40 and 41.

Phenols: references 34, 36, 37, 39 and 41.

Benzoic acids: references 38, 41 and 42.

Sulfonic acids: reference 39.

Conductivities

Although this report is not directly concerned with conductivity data, such data are often of considerable use in connection with the kinds of potential data discussed earlier and should not be entirely ignored here. Several of the references cited in the preceding section also give some conductivity data. Results of other conductivity measurements are cited in references 3, 17, 43-61. Results of some of these investigations have yielded association constants for various ion pairs. Several of these investigations (especially those of Fuoss) have been concerned with mixed solvent systems of which acetonitrile was one component. A recent paper by Cunningham, Evans and Kay⁶² reports some interesting data on transport properties.

Miscellaneous

Cruse, Goertz and Petermoller⁶³ have made measurements on cells of type $\text{Hg}|\text{Hg}_2\text{X}_2|\text{X}^-$ in $\text{CH}_3\text{CN}|\text{AgX}|\text{Ag}$, with uncertain results. Ulich and Spiegel⁶⁴ made emf measurements with sodium amalgam drop electrodes with several solvents, including acetonitrile. Results for acetonitrile were not in accord with those for the other solvents. Later measurements by Spiegel and Ulich⁶⁵ with lithium amalgam dropping electrodes in several solvents (including acetonitrile) led to activity coefficients for Li in the amalgam and for LiCl in solution.

Korchinski⁶⁶ has investigated the electrocapillarity of mercury and obtained information about adsorption of ions from acetonitrile.

In addition to sources of solubility data already mentioned, we call attention to recent work on silver halides by Juehrs, Iwamoto and Kleinberg⁶⁷.

Mishchenko and Sukhotin⁶⁸ have reported heats of solution of NaI in CH_3CN .

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